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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Photographic Gelatin Hardening Baths

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester 4, New York, United States of America (Assignees of HARRY CHRISTIAN BADEN, CHARLETON CORDERY BARD and JAMES MARVIN SEEMANN), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to photographic processing and more particularly to a method of hardening gelatin and to photographic processing solutions for use in the method.

According to the present invention there is provided a method of hardening gelatin comprising bathing the gelatin with an aqueous solution having a pH between 2 and 10 and containing succinaldehyde and optionally, either formaldehyde or mucochloric acid, an alkali metal sulphate, an alkali metal bromide and essentially one or more succinaldehyde polymerisation inhibitors which may be dioxan, ascorbic acid, acetyl acetone, an aliphatic alcohol containing between 6 and 15 carbon atoms, an aromatic sulphinic acid, kojic acid or an aminoaliphatic acid having from 2 to 4 carbon atoms.

There is further provided a gelatin hardening bath comprising between 0.5 and 50 grams/litre of succinaldehyde or a succinaldehyde supplying compound, as herein described, between 1 and 200 ml/litre of formaldehyde as a 37% aqueous solution, between 100 and 200 grams/litre of an alkali metal sulphate, up to 50 grams/litre of an alkali metal bromide, and one of more succinaldehyde polymerisation inhibitors which may be dioxan, ascorbic acid, acetyl acetone, an aliphatic alcohol containing between 6 and 15 carbon atoms, an aromatic sulphinic acid, kojic acid or an aminoaliphatic acid having from 2 to 4 carbon atoms, and sufficient free acid or alkali to set the pH to between 2 and 10.

It is advantageous in preparing the hardening baths of the invention that they be prepared from a succinaldehyde supplying compound or precursor such as dimethoxytetrahydrofuran or diethoxytetrahydrofuran which is hydrolyzed to succinaldehyde in aqueous solution at a low pH and then mixed with formaldehyde and other additives if required. Supplying of the succinaldehyde to the hardener composition via the precursor offers advantages in handling over using succinaldehyde itself in preparing these hardening compositions.

When these succinaldehyde-formaldehyde hardening compositions, particularly those prepared by in situ hydrolysis of a succinaldehyde precursor, are used without a polymerisation inhibitor they have a tendency to produce a precipitate after standing or after use upon photographic film. The precipitate is presumed to be the polymerization product of succinaldehyde. Such polymerization appears to be induced by oxidation. The polymer causes spots on processed film having the appearance of dirt. Hence the objectionable material is called "polymeric dirt". This dirt can plug recirculation line filters and form undesirable coatings on the processing apparatus.

Photographic succinaldehyde-formaldehyde hardening solutions having good characteristics are obtained when one or more of the succinaldehyde polymerisation inhibiting materials is incorporated therein. These solutions are particularly useful for pre-hardening photographic materials prior to development.

The prehardening compositions in accordance with this invention are composed of aqueous solutions having a pH of 2 to 10 and containing the following:

[*Price 4s. 6d.*]

1. Succinaldehyde (or its precursor) 0.5—50 gram/litre
2. Formaldehyde (37% solution) 1—200 ml/litre
3. Alkali metal sulphate 100—200 gram/Litre
4. Alkali metal bromide 0—50 gram/litre [pH 2 to 10]
5. (Plus) a polymerisation inhibiting proportion of a material selected from the following:

A. Dioxan
B. ascorbic acid
C. acetyl acetone
D. the C_6—C_{15} aliphatic alcohols
E. aromatic sulphinic acids
F. kojic acid
G. the amino aliphatic acids of 2—4 carbon atoms.

Generally these inhibitors will be used in a proportion of 0.1 to 20 grams per litre of the hardener composition. In the case of the aliphatic alcohols, lower proportions have been found to be effective. For instance, concentrations of octyl alcohol down to as low as 0.01 gram/litre have been found useful. In many cases useful proportion has been limited to correspond to the water solubility of the material used.

Of the inhibiting materials listed, the aromatic sulphinic acids have been found to be especially useful. Some acids useful in hardener compositions are the following: benzene sulphinic acid, para-toluenesulphinic acid, salicyl sulphinic acid, acetamide benzene sulphinic acid, naphthalene sulphinic acid, and chlorbenzene sulphinic acid. Of the aliphatic alcohols octyl alcohol has been found to be especially useful as an inhibiting material, but other alcohols containing from 6 to 15 carbon atoms are useful in this connection. Of the simple amino acids the representative compound glycine has been found to be particularly effective. The compositions in accordance with this invention have shown themselves to be useful in continuous processes for developing photographic film due to their effectiveness as prehardeners and their freedom from the formation of precipitate or dirt in the prehardening operation.

In preparing hardener compositions using dimethoxy or diethoxy tetrahydrofuran as a succinaldehyde precursor, that material is conveniently hydrolyzed to succinaldehyde in all or the greater part of the water employed in preparing the hardener composition. Hydrolysis proceeds at a practical rate at a pH of less than 3 and a temperature within the range of 25—60° C. The final equilibrium concentration of the DMTF drops to less than 0.1 gram/litre. After the hydrolysis the various other constituents which may be required in the hardening composition are normally added although as the rate of hydrolysis is not usually affected by the presence of the other constituents they may be added at the beginning providing they do not prevent the pH being maintained below 3 during the hydrolysis operation.

These hardener compositions can also be used as hardeners anywhere in a photographic processing sequence and can be used in black-and-white and in colour processes. They are however particularly useful as prehardeners in colour processes at elevated temperatures.

The following examples illustrate the preparation of prehardener compositions in accordance with this invention:

Example 1

800 ml. of water at 90° F was used to dissolve 4.30 ml. of dimethoxytetrahydrofuran, 5.41 ml. of 18 Normal sulphuric acid and 0.5 gram of the sodium salt of para-toluenesulphinic acid. This solution was stirred for 10 minutes at 90° F whereby the DMTF became hydrolyzed to succinaldehyde and methanol. 153 grams of sodium sulphate and 2 grams of sodium bromide were then added and the composition was mixed for 20 minutes. There was then added 20 grams of sodium acetate and 27 ml. of formalin, the volume was then adjusted to one litre by the addition of water and the pH was adjusted to 4.8 at 80° F. The composition prepared was used as a prehardener for photographic films containing gelatin-silver halide photographic emulsions and was found to be an effective prehardener when used to harden film prior to the processing of the film in the developing baths. This prehardener composition had the unique property of hardening the gelatin emulsion at a low pH and was very effective within the pH range of 4—5.

Example 2

A solution was prepared in 800 ml. of water at 90° F of 2.7 grams of succinaldehyde, 0.5 gram of paratoluenesulphinic acid sodium salt, 5.41 ml. of 18 Normal sulphuric acid, 153 grams of sodium sulphate and 2 grams of sodium bromide. This mixture was mixed for 20 minutes whereupon there was added 20 grams of sodium acetate and 27 ml. of formalin, the volume was then brought to one litre with water, the pH was adjusted to 4.8 at 80° F and the resulting prehardener composition was used for hardening photographic film containing a gelatin-silver halide emulsion layer thereon prior to introducing the film into the developer. Good prehardening effect was obtained and it was found that no polymeric dirt had formed either in the processing of photographic film using the composition of this example or in the processing described in the preceding example.

Example 3

A solution was prepared in 600 ml. of water at 90° F of 0.10 ml. of octyl alcohol,

4.30 ml. of dimethoxy-tetrahydrofuran, and 5.41 ml. of 18 Normal sulphuric acid. This solution was mixed for ten minutes after which time 153 grams of sodium sulphate and 2.0 grams of sodium bromide were added. The solution was then stirred for 20 minutes, whereupon 20 grams of sodium acetate and 27 ml. of 37% formalin and sufficient water to make the final volume 1 litre were added. The pH was adjusted to 4.80. This solution exhibited a good prehardening effect and could usefully be employed without the build-up of polymeric dirt on the film or apparatus.

WHAT WE CLAIM IS:—

1. A method of hardening gelatin comprising bathing the gelatin with an aqueous solution having a pH between 2 and 10 and containing succinaldehyde and optionally, either formaldehyde or mucochloric acid, and alkali metal sulphate, an alkali metal bromide and essentially one or more succinaldehyde polymerisation inhibitors which may be dioxan, ascorbic acid, acetyl acetone, an aliphatic alcohol containing between 6 and 15 carbon atoms, an aromatic sulphinic acid, kojic acid or an aminoaliphatic acid having from 2 to 4 carbon atoms.

2. Method as claimed in Claim 1 wherein the polymerisation inhibitor is present in an amount between 0.01 and 20 grams per litre.

3. Method as claimed in Claim 2 wherein the polymerisation inhibitor is present in an amount between 0.1 and 20 grams per litre.

4. Method as claimed in any of the preceding claims wherein the polymerisation inhibitor is octyl alcohol.

5. Method as claimed in any of the preceding claims wherein the polymerisation inhibitor is *p*-toluene sulphinic acid.

6. Methods of hardening gelatin as herein described.

7. Gelatin whenever hardened by the method of any of the claims 1 to 6.

8. A gelatin hardening bath comprising between 0.5 and 50 grams/litre of succinaldehyde, between 1 and 200 ml/litre of formaldehyde as a 37% aqueous solution, between 100 and 200 grams/litre of an alkali metal sulphate, up to 50 grams/litre of an alkali metal bromide, and one or more polymerisation inhibitors which may be dioxan, ascorbic acid, acetyl acetone, an aliphatic alcohol containing between 6 and 15 carbon atoms, an aromatic sulphinic acid, kojic acid or an aminoaliphatic acid having from 2 to 4 carbon atoms, and sufficient free acid or alkali to set the pH to between 2 and 10.

9. Gelatin hardening baths containing succinaldehyde or a succinaldehyde supplying compound and one or more polymerisation inhibitors, as herein described.

10. Method of making a gelatin hardening bath as claimed in Claim 8 comprising preparing an aqueous solution of dimethoxy or diethoxy tetrahydrofuran to contain between 0.5 and 50 grams per litre, reducing the pH to less than 3 while holding the temperature in the range 25 to 60° C, adding the remaining components of the bath while keeping the pH in the range 2 to 10.

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